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# THE DISTRIBUTION OF SELENIUM IN ALBERTA

by

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University of Alberta,
Edmonton, Alberta.

April, 1939.

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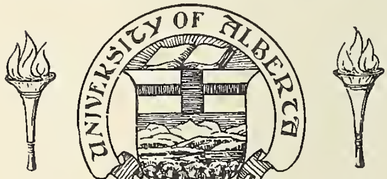

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Thesis
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# THESIS

# THE DISTRIBUTION OF SELENIUM IN ALBERTA

Submitted in partial fulfilment of the
requirments for the degree of Master of Science.

By

Walter E. Harris B.Sc.
Under the direction of Dr. O.J. Walker.
In the Department of Chemistry

Time devoted to thesis work: 5.3 months out
of 7.0 months devoted to M.Sc. work.

Time is proportioned on basis of 7.0 months
for an academic year and 4 full courses representing
one academic year's work.

EDMONTON, ALBERTA. April, 1939.

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# THE DISTRIBUTION OF SELENIUM IN ALBERTA

## INTRODUCTION

In certain of the American States on the east side of the Rocky Mountains, evidence was obtained early of a number of mysterious diseases afflicting animals and to these were given the names "Alkali Disease", "Blind Staggers", etc.

Marco Polo (5) in the story of his travels through the province of Su-Chau may have been referring to these same diseases. The following excerpt is taken from his book of travels:

> "......Travelers, however, dare not visit those mountains with any cattle but those of the country, for a certain plant grows there which is so poisonous that cattle which eat it lose their hoofs. The cattle of the country know it and eschew it......"

The mountains to which he refers are probably in China and these observations were made sometime in the thirteenth century.

Madison, (3) an army surgeon, in 1856 at Fort Randall probably wrote the first scientific report on record of the disease. He observed in the cavalry horses a swelling and suppuration of the sheath, tenderness and inflammation of the feet, loosening of the hoofs and the loss of the hair from the manes and tails. He also correctly suggested that the toxic factor was to be found in the plants growing in the ravine in which the horses were getting food.

This disease was misnamed "alkali poisoning" by the early settlers on the Great Plains due to its supposed relation with the high mineral content of the water in these regions. Work at the South Dakota State College in 1912-13by Larsen and Bailey (1) (2) disproved any association of the alkali disease to the alkali waters. At the present time two different types of poisoning are recognized so the name "alkali poisoning" will quite probably be retained to designate the type to which it was originally applied.

Investigations conducted by the United States Department of Agriculture in conjunction

with some State Experimental Stations have shown that most of the states of the Great Plains and Rocky Mountain area,are being adversely affected by toxic vegetation in certain endemic areas.

The cause of the disease "alkali poisoning", and its related disorder "blind staggers", was not definitely proven until after Franke and his associates (9) in 1929 started their work on the problem at South Dakota State College. They conducted feeding trials on rats with "alkalied" grains and were able to produce typical symptoms of these diseases. The possibility that arsenic, thallium or some of the other less common elements might be causing the disease was disucssed. In 1931 Knight suggested that selenium might be present in the toxic vegetation and in 1933 Robinson (18) showed on analysis that a toxic wheat contained 12 PPM[#] of selenium. In connection with the last part of the quotation by Marco Polo (Page 1) it should be noted that Beath (6) has observed that in a state of nature animals tend to avoid toxic seleniferous plants while imported stock are often poisoned due to lack of experience with the toxic plants. Since that time

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[#] PPM Parts per million parts of sample

feeding experiments have shown that the effects of naturally toxic grains are similar to those of diets containing inorganic salts of selenium.

Selenium poisoning has been divided(3) into two general classes: the chronic type known as "alkali disease," and the acute type known as "blind staggers." These diseases manifest themselves in the ordinary farm animals such as cows, horses, pigs and chickens.

The severe type of poisoning known as "blind staggers" is the result of eating food containing large amounts of selenium, and seems to be most prevalent in Wyoming. Beath (6) (11) describes the symptoms in this manner. In the first stages ofthe disease there is a slight impairment of vision and the animal seems unable to JUDGE distances correctly. In the intermediate stages, the blindness is more pronounced. The animal wanders about aimlessly and when a solid object is met with tries to push the object aside rather than go around it . It develops a depraved taste which is manifested by the tendency to chew wood, bone and metallic objects. The last stages of the disease are

shown by varying degrees of paralysis, evidence of abdominal pains, grating of the teeth, salivation and grunting. Beath (12) has also observed that the animal may give no outward sign of illness for months after grazing on the toxic plants. Then apparently sound and healthy animals suddenly go "off feed", pass bloody urine and rapidly lose weight. Death usually results in from 1-6 days after the breakdown occurs.

"Blind staggers" have been treated by Beath and Draize (13) by thehypodermic administration of small amounts of strychnine sulfate and drenching with large amounts of warm water.

The Symptoms of "alkali disease" in contrast to those of "blind staggers" are developed as a result of eating a diet relatively low in selenium over a fairly long period of time. The mildest form of poisoning is shown merely by retardation in the rate of growth.

With larger amounts of selenium in the diet the animal shows loss of appetite, becomes emaciated and nervous and the hair becomes roughened. Loss of hair from the tail and other parts of the body is followed by soreness of the feet. A gradual

separation of the wall of the hoof may occur and a new hoof may start to grow out. As this new hoof grows the old one is gradually pushed down and finally discarded. Due to the soreness of the feet the animal finds it increasingly more difficult to move about and often dies of starvation and thirst. Some cattle rest on their knees while they are grazing to avoid standing on their feet. Erosion of the joints of the long bones causes them to become stiff and lame.

The young may be born with all the prominent symptoms of alkali disease such as lameness, loss of hair from the body and deformations or abnormal developments of the hoofs. They may later be adversely affected by the transmission of selenium through the milk of the selenized mother.

In the case of poultry, the adult seems to be little affected by toxic grains but the main effect shows up in the eggs. The fertility remains high but the baby chicks hatched out are deformed. The main deformitiesare in the feet, head, and neck and there may be lack of full-sized upper beak, and other abnormalities such as missing eyes, feet or wings. Mortality is high among the chicks and those

that remain alive are weak and have a wiry down in place of the normal fluffy coat.

The possibility of injury to the health of people residing on seleniferous areas has been investigated by Smith and Westfall (32) but the question is still an open one.

On post-mortems carried out on animals which have died the liver is found to be the seat of the most important pathological changes. It becomes atrophied and shows a tendency toward fatty degeneration. Both the liver and the kidneys are inclined to be hemorrhagic. The heart is damaged in the severe cases. Franke (9) and Schneider (8) have shown in experiments on laboratory animals that anemia is often a prominent feature of the disease.

Gmelin appears to have been the first to investigate the effects of selenium on animals. He found that the salts of selenium were poisonous and that they produced a deposit of the element in the tissues. Physiologically, the reduction of the selenium salts to the metallic state seems to be the means of defense of the organism (8) (16).

Franke (17) has shown that selenium from different sources varies in toxicity. Thus selenium as it occurs in wheat is more toxic than that to be found in corn. He gives the following order of the toxicities of selenium: wheat > corn > barley > selenate > selenite. A high degree of correlation has been found between the toxicity of the involved food and the selenium content.

No definite toxicity levels have been established but the following results have been obtained by various workers:

Moxon (3) found that 5 PPM fed to hens did not appreciably affect the hatchability of the eggs but the chicks had a wiry down. No apparent effects are shown by 2.5 PPM of selenium. Chicks fed 8 PPM show a decrease in the rate of growth but a concentration of 4 PPM had no significant effect.

Franke (17) states, in general, that 10 PPM causes pronounced reduction of food consumption and 5 PPM prevents normal growth. Munsell(14) establishes 4 PPM as a tolerance limit in foodstuffs for lower animals.

Byers (33) states that the normal quantity found in soils which are considered seleniferous is generally from 1-6 PPM.

Although all plants growing upon a seleniferous soil absorb selenium to some extent there appear to be certain plants more prone to do so than others. Even for a given species of plant there is no direct quantitative relationship between the selenium present in the soil and that absorbed by the plants (20). In the main the selenium to be found in a plant depends upon the two factors:

1- The kind of plant.

2- The forms of selenium present in the soil and the total quantity present.

Miller and Byers (21) have classified plants into three broad groups in relation to their tolerance of selenium in the soil.

a- Plants that absorb selenium readily belong mainly to the genus Astragalus. The presence of these plants on a soil often suggests the presence of selenium in the soil upon which they are growing. Since they grow vigorously even with a very high content of selenium it is quite probable that

selenium is of importance in their physiological processes.

b- Plants that can absorb only moderate amounts have a rather low tolerance for selenium and are killed when too much is absorbed. The common cereals are included in this group.

c- Plants having a very limited tolerance for the element are either absent or grow very poorly on soils containing much selenium. Buffalo grasses and grama grasses are included in this group.

Hurd-Karrer (22) (23) has shown that there is a parallel variation in the rates of absorption of the elements sulfur and selenium from the soil. She suggests that this direct functional relationship is explainable on the basis that since sulfur and selenium are adjacent in the periodic table the plant does not discriminate between them in the processes of absorption. This parallel relationship permits prediction of the relative selenium absorption by crops whose sulfur requirements are known. On the hypothesis that additional sulfur added to a soil will be absorbed in preference to selenium, Hurd-Karrer found that the addition of sulfur either elemental or

in combination may be successfully used in controlling the absorption of selenium by plants. Martin (24) also reports that the addition of sulfate to the nutrient solution of plants tends to reduce the accumulation of the selenium in the plant.

The results of Hurd-Karrer's work are not applicable to soil conditions as they exist in seleniferous areas because in general the sulfates are very high (3) (20). Further the cost of application of sulfate to the soil of such areas would be prohibitive. Byers (25) suggests that irrigation is a possible solution of the problem. There is a marked decrease of selenium in plants when grown in humid soils or soils under irrigation. This applies particularly when there is adequate underdrainage.

The most effective cause of variation in the plant content in individual species is probably to be found in the differences in the forms present in the soil. The elemental form is essentially absent from the soil. If it were present it would be expected to follow the general behavior of sulfur and be converted into selenites. It is of no importance as far as the plant is concerned. Williams and

Byers (26) have studied the forms of selenium to be found in the soil and have found four general types.

a- Pyritic selenium. This is relatively unimportant, except for its bearing upon the problem of sources of selenium, because in this form it is not available to the plant. In the examination of several hundred samples of pyritic ores Williams (27) found no case in which selenium was absent so it follows that if a soil contains pyrites it will necessarily contain selenium.

b- Insoluble inorganic selenites. The compound usually present in the soil to the larges extent is very slightly soluble in water and is though to be a basic ferric selenite. In an attempt to synthesize a compound having the required properties Byers obtained a basic ferric selenite of the approximate composition $Fe_2^{''}(OH)_4^{''}SeO_3^{''}$ by allowing an extremely dilute solution of selenite to react with one of ferric chloride. In this precipitate the ratio of iron to selenium is not constant. There is incomplete precipitation of the selenium when the mixture is sufficiently acid.

c- Soluble inorganic selenium compoun Twenty per cent of the soils examined by Williams and Byers were found to contain water soluble selenium

compounds. This is probably present in the form of selenates usually calcium selenate. The selenium present in this form is readily available to the plant.

d- Organic selenium compounds. It has been shown by a number of workers (9) (28) (29) that the greater portion of the selenium content of the plant is to be found in the protein fraction. Jones, Horn and Gersdorff found that when gluten from toxic wheat is completely hydrolysed the selenium containing compound is largely concentrated in the leucine fraction of the amino acids. The properties of the selenium compound present are apparently very similar to those of the amino acids associated with it. They conclude that the selenium in toxic grain is an integral part of the protein.

In the soil, these compounds DECOMPOSE through decay as do other proteins and the resulting selenium-bearing products are water soluble. These soluble organic compounds are readily absorbed by plants. This decay of plant material to give soluble selenium compounds is very important, practically. Of considerable importance to the problem are the "converter plants" (3) (31) which are seleniferous plants apparently able to utilize selenium in forms

not available to ordinary crop and grass plants. Through their decay they promote the selenization of other plants by concentrating the selenium in an available form in the surface soil.

The findings of the United States Department of Agriculture in conjunction with some of the State Experimental Stations show that some of the states adversely affected by endemic areas of selenium in vegetation are bordering on Alberta. In veiw of this fact it was decided to investigate the possibility of Alberta being similarly affected by vegetation made toxic by selenium. The work done is largely in the nature of a preliminary survey since no field work was undertaken. In the survey wheat, to a large extent, was used as an indicator of the presence or absence of selenium because it is the most generally grown and most easily obtained Material to examine. Soils could have been used but the presence of selenium in a soil is not necessarily an indication that it is being absorbed by plants growing upon it.

## DISCUSSION OF METHODS OF ANALYSIS

The methods in use or proposed for the detection or estimation of selenium were investigated with a view to adapting one to the analysis of wheat and soils for selenium in this research.

Any reasonably accurate and rapid method of analysis at the present time seems to depend upon the distillation of the selenium as the tetrabromide and the resultant estimation, by color or weighing, of the selenium AFTER reduction, usually with sulfur dioxide. The method proposed by Robinson (34), with modifications, seems to be the one used almost exclusively at the present time.

The halogen acids have the effect of forming volatile halides with trivalent arsenic, tetravalent selenium and germanium and are volatilized when the acids are boiled. Thus when hydrobromic acid is distilled there results in the distillate a group of volatile elements called the selenium group, comprising the three elements selenium, arsenic and germanium. Hydrobromic acid causes these elements to distil over completely in their lower valence states

even when they were originally present in their higher valencies. With hydrochloric acid the volatilization is not nearly so complete. To ensure the selenium coming over quantitatively it must be in or converted into the tetravalent state. This is accomplished by the addition of excess bromine. The excess distills over at a low temperature and then the hydrobromic acid reduces the selenium from the hexavalent to the tetravalent condition. The selenium from such a distillate can be quantitatively precipitated and separated from the other elements present merely by the addition of reducing agents such as sulfur dioxide and hydroxylamine hydrochloride. The selenium is reduced from the hexavalent or tetravalent state to the red elemental form.

$$SeBr_4 + SO_2 + H_2O \longrightarrow H_2SO_4 + HBr + Se\downarrow$$

Robinson (35) applied the above principles to the determination of selenium in wheat and soils. Without prior treatment he distilled the hydrobromic acid and bromine directly from soils and extracted ashed wheat samples with a mixture of hydrobromic acid and bromine. Precipitation of the selenium was by sulfur dioxide and hydroxylamine hydrochloride, and the precipitate after digestion was filtered and

weighed. During the ashing of the Plant materials as in the above there is the constant danger of volatilization of part of the selenium through the use of too high temperature.

Later Robinson (34) extended and improved his work to include the estimation of small amounts of selenium colorimetrically. Before distillation he oxidized the organic matter through the use of an ignition with magnesium nitrate or magnesium oxide or by digestion with hydrogen peroxide or sulfuric acid as in the ordinary Kjeldahl process. He determined the selenium content of wheats from various parts of the world (36)by ashing the gluten fraction of the grain with magnesium nitrate and potassium hydroxide at a temperature of 500° C.

Byers (20) found that the Kjeldahl procedure as proposed by Robinson (34) was very satisfactory and made several thousand determinations through its use.

Dudley and Byers (37) adapted the procedure to the determination of selenium in animal matter and in urine. A sample of the order of 50 grams was covered with concentrated nitric acid for two or three days and then a quantity of hydrogen peroxide was

added along with a fairly small quantity of sulfuric acid. The sample was then taken to dryness and distilled with hydrobromic acid and bromine as before.

Williams and Lakin (38) proposed a modification to the method of Robinson (34) which made the determination much more rapid. They digested the sample with a mixture of sulfuric and nitric acids and drove off the excess nitric acid at a temperature below 120°C. Distillation with hydrobromic acid and bromine was carried out as before. In his most recent work Byers (25) has used this method in a large number of samples.

Curl and Osborn (39) modified the wet digestion procedure in one important respect, that of adding mercury as a catalyst. That mercury seems to reduce the volatility of selenium has been observed by Osborn and Krasnitz (40). Moxon has indicated that he was able to get higher selenium recovery with the addition of a mercury catalyst. Using this method the samples can be digested quickly without the necessity of careful control of temperature as in previous procedures (37) (38). It was found in this laboratory that a loss of about 25 per cent of the selenium present occured during the digestion stage.

The above workers make use of sulfur dioxide and hydroxylamine hydrochloride in the precipitation of the selenium after distillation. In this precipitation various workers in other parts of the world have used in conjunction with sulfur dioxide a number of other substances serving the same purpose as hydroxylamine hydrochloride.

a- Hydrazine hydrate, hydrazine sulfate (41).

b- Formaldehyde (42).

c- Thiourea (43) (44).

d- Diphenylhydrazine (45).

e- Phenylhydrazine (46).

f- Acetone sulfite (47).

Other methods have been proposed for the detection and estimation of selenium.

In the presence of selenious acid pyrrole yields a deep blue coloration (48) (49). This serves for the detection of selenium. With the purpose in mind of making it quantitative some experimental work was carried out on this method. A set of standards containing from 0.0 to 0.1 mg of selenium in a small volume were made up from a standard solution of selenium containing 0.1 mg

of selenium per cubic centimetre. To these were added 1 cc of 5 per cent ferric chloride solution and the volume made up to 10 cc with phosphoric acid. Five to ten drops of 1 per cent pyrrole in alcohol were then added. After a few minutes a blue coloration began to appear. Maximum depth of color developed after several hours and at that time the depths of color developed were compared in the tubes of a Bausch and Lomb colorimeter. A sample containing one amount of selenium, i.e. 0.02 mg, was set and then compared with standards containing varying amounts. A second set of standards was made up later with a range of 0.0 to 0.01 mg of selenium and similar color comparisons carried out. The results of the comparisons are shown below in Table 1.

In the case of the first set of standards the one containing no selenium was not comparable with the others since the color was a dirty yellow instead of a blue.

## TABLE 1

| Colorimeter Reading 0.02 mg MM | Selenium in Comparison Cup MG | Reading with Comparison Cup MM |
|---|---|---|
| 18 | 0.04 | 14 |
| 18 | 0.06 | 21 |
| 18 | 0.08 | 21 |
| 18 | 0.1 | 22 |
| 30 | 0.04 | 24 |
| 30 | 0.06 | 33 |
| 30 | 0.08 | 32 |
| 30 | 0.1 | 35 |
| Second Set Standards 0.002 mg | | |
| 6.5 | 0.0 | 15 |
| 6.5 | 0.004 | 20 |
| 6.5 | 0.006 | 19 |
| 6.5 | 0.008 | 38 |
| 6.5 | 0.01 | 27 |
| 11 | 0.0 | 30 |
| 11 | 0.004 | 37 |
| 11 | 0.006 | 32 |
| 11 | 0.008 | -- |
| 11 | 0.01 | 38 |

It will be seen from these data that there is no definite relationship between the color developed and the amount of selenium in the test. For this reason the method was not considered further.

The reaction between selenious acid and ammonium thiocyanate has been most recently studied by Ljung (50) and Hall (51). In the presence of

considerable hydrochloric acid a yellow compound is precipitated which has the formula $(HCNS)_2H_2SeO_3$ (52). When the solution is heated decomposition of this compound takes place to give metallic selenium. The equation

$$2H_2SeO_3 + HCNS \longrightarrow 2Se\downarrow + CO_2 + SO_4^{=} + H^{+} + NH_4^{+}$$

shows how the reaction might take place. Ivanov (52) found that sulfur was always precipitated with the selenium.

In considering this method the fact should be kept in mind that this identification step depends upon earlier steps in which the selenium has been associated with bromine and sulfur dioxide. At this step one would be left with a solution containing a large excess of bromine. The ammonium thiocyanate instead of reacting with the selenium would be destroyed by the bromine. On the other hand, if one first destroys the bromine with sulfur dioxide, the unavoidable excess of sulfur dioxide precipitates the selenium so that no reaction can take place between it and the thiocyanate. These things more or less eliminate it from practical consideration.

Pierson (53) (54) has recommended the use of mercurous chloride in the separation and detection

of selenium and other easily reduced elements. The general equation for the reaction is as follows,

$$HgX + MX \longrightarrow HgX_2 + M$$

This reaction is essentially unidirectional and proceeds rapidly even with the highly insoluble mercurous halides. The metals thrown out of solution are colored and this color absorbed on the white mercurous chloride affords a means of detection and estimation.

While this method is a very sensitive one the same difficulties are met with in attempting to adapt it as in the preceding method. Either the mercurous chloride will be rendered useless by the bromine or the selenium is precipitated too soon by the sulfur dioxide.

Horn (55) used a colorimetric procedure he had found to be partially satisfactory from a quantitative point of veiw. He used it mainly as a negative test. Essentially it involved a Kjeldahl digestion of the sample with mercuric oxide catalyst, with the addition later of a small amount of codeine sulfate to a portion of this digest. A green color changing to a blue develops in the presence of selenium.

Experimental work on this method of estimation indicated that the following conditions had to be observed if reproducible colors were to be obtained.

1- With 0.1 mg of selenium in 10 cc of sulfuric acid a minimum of 0.004 g of codeine sulfate had to be added. The maximum color is developed in about 10 minutes.

2- The reaction must be carried out in the cold. With warm sulfuric acid a brown color is developed. This brown color also develops on allowing the solution to stand for a day at room temperature.

3- The presence of water in the sulfuric acid prevents the full development of color. A slight trace of water seemed to be desirable, however, probably due to the action of too concentrated acid on the codeine sulfate.

4- Saturation of the sulfuric acid with sulfur dioxide eliminates practically all of the off color samples.

It was hoped to be able to isolate the selenium by the distillation procedure of Robinson (34) ( See page 17 ) and having obtained the precipitate on an asbestos mat, go on from there to estimate it quantitatively with codeine sulfate and sulfuric acid.

The immediate problem is then to get the metallic selenium on the mat into solution in concentrated sulfuric acid.

Mellor (56) states that selenium dissolves in concentrated or fuming sulfuric acid, but efforts to dissolve selenium in concentrated sulfuric acid were unsatisfactory. Nitric acid dissolves it readily but after driving off the nitric acid with sulfuric acid, comparable colors with standards could not be obtained. Small amounts of nitrates must persist to interfere with the test. Hot sulfuric acid containing bromine dissolves the selenium fairly readily but it was not found possible to completely destroy the excess bromine with sulfur dioxide. A yellowish color remains even after prolonged bubbling of the sulfur dioxide through the solution. Even at the beginning the disappearance of the bromine is very slow.

Apparently if the codeine sulfate method is to be used it will have to be in conjunction with a sulfuric acid digestion of the sample. Several digestions were carried out, in the manner of a Kjeldahl digestion with sulfuric acid, on 20 gram samples of wheat. This digestion took about 20 hours

with the aid of a mercury catalyst. The total volume of digest obtained was generally about 150 cc. To 10 cc portions of this digest codeine sulfate was added and the colors compared with those of standards. The sulfuric acid used for standards had to be saturated with mercuric sulfate because mercury salts give a yellow color with codeine sulfate. A yellow color originally present in the digest was not intensified by the addition of codeine sulfate.

In order to find the elements interfering with the test, codeine sulfate was added to 0.02 mg of selenium in 10 cc of sulfuric acid, saturated with sulfur dioxide and mercuric sulfate, to which had been added about 0.25 g of various ingredients. Color comparisons were carried out after 10 minutes and after 2 hours.

Those compounds showing interference when 0.25 g was used were again tested with the use of 0.002 g in sulfuric acid containing no selenium. Color comparisons were carried out as before.

The results of these tests are tabulated in Table 2.

## TABLE 2

| 0.25 g Ingredient Added | Color<br>10 minutes | Comparison<br>2 hours |
|---|---|---|
| Standard | dark green | dark green |
| Chromium sulfate | no interference | no interference |
| Zinc sulfate | no interference | no interference |
| Nickel sulfate | no interference | no interference |
| Molybdic acid | reddish purple | very dark color |
| Manganese dioxide | greenish blue | dark green |
| Ferric alum | yellow | light yellow |
| Boric acid | no interference | no interference |
| Sodium carbonate | no interference | no interference |
| Arsenious oxide | no interference | no interference |
| Magnesium sulfate | no interference | no interference |
| Strontium sulfate | no interference | no interference |
| Tungstic acid | no interference | no interference |
| Bismuth sulfate | no interference | noninterference |
| Titanium sulfate | no interference | no interference |
| Cadmium sulfate | no interference | lighter (slight) |
| Copper sulfate | no interference | lighter ( slight) |
| Lead sulfate | no interference | lighter (slight) |
| Water glass | Hinders full development of color. | |
| Phosphoric acid | no interference | no interference |
| Telluric acid | no interference | very dark blue |
| Cerium sulfate | lighter (slight) | no interference |
| Thallium sulfate | no interference | no interference |
| Zirconium sulfate | no interference | no interference |

| 0.002 g Ingredient Added | | |
|---|---|---|
| Standard (no Se.) | yellow | yellow |
| Molybdic acid | no interference | # |
| Manganese sulfate | lighter green | lighter * |
| Ferric alum | no interference | no interference |
| Titanium sulfate | very light * | lighter * |
| Telluric acid | lighter | slight pink |

#- 0.02 mg of selenium were added to this sample before two hours and it turned a very dark reddish purple. An attempt to make a set of standards allcontaining o.004 g of molybdic acid showed that molybdenum would interfere with the test.

* Refers to the yellow of the standard.

It was concluded that the elements molybdenum, manganese, titanium and tellurium interfere with the test.

The codeine sulfate method was not used because of the following disadvantages:

1- A colorless digest is very difficult to obtain without the use of too large quantity of sulfuric acid. A yellow is retained which interferes with the quantitative estimation of small quantities.

2- Although 0.001 to 0.0005 mg of selenium can be detected by this method, due to the fact that only a portion of the whole digest is used the sensitivity is reduced to about 1 PPM.

3- The elements mentioned above may interfere with the test. In the case of wheat there is probably no real danger of these elements being in large enough quantities to interfere with the test.

## EXPERIMENTAL METHOD

It was decided to use the method of Robinson (34) with the modifications suggested by Curl and Osborn (39). This method was chosen because it is readily adapted to routine determination of selenium. The manipulations are not difficult and the final estimation of the element is free from practically any interference. The order of accuracy provided by this method is well suited to the purposes of this investigation. The minimum visible amount of selenium is of the order of 0.002 or 0.001 mg. This in a sample of 10 grams gives readings as low as 0.1 PPM.

In general a sample of wheat or soil of 10 grams was used with occasionally one of 30 gram size.

The sample was put into a round bottom distilling flask containing a mixture of 50 cc concentrated sulfuric acid Along with 12.5 cc of nitric acid per gram of sample. Half a gram of mercuric oxide was added as a catalyst. After being allowed to stand for about half an hour it was heated until the nitric oxide and the nitric acid were driven off and the solution turned to a dark brown. The amount of nitric acid used was varied throughout the year from

10 to 20 cc per gram of sample but in the end it was found with a digestion time of three or four hours and 12.5 cc per gram a good digest could be obtained with but a small amount of waxy material.

The digestion and distillation were carried out in the fume cupboard fitted up as shown in Fig.1. As can be seen, provision is made for withdrawing the fumes from each flask.

The digest was allowed to cool and 100 cc of 45% hydrobromic acid and 1 or 2 cc of bromine were added. This mixture was distilled until 75 cc had come over, care being taken that a small amount of bromine comes over in the first portion of the distillate.

As the distillation involves the use of hydrobromic acid and bromine, both of which speedily attack the corks used in an ordinary distillation set-up, it was found necessary to use the distillation apparatus shown in Fig. 2. This apparatus is the same as that devised by Robinson (34). Two complete sets and extra flasks were obtained from the Emil Greiner Co., New York.

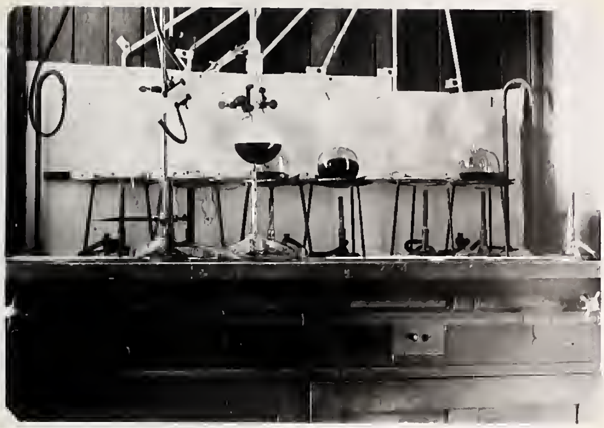

Figure 1

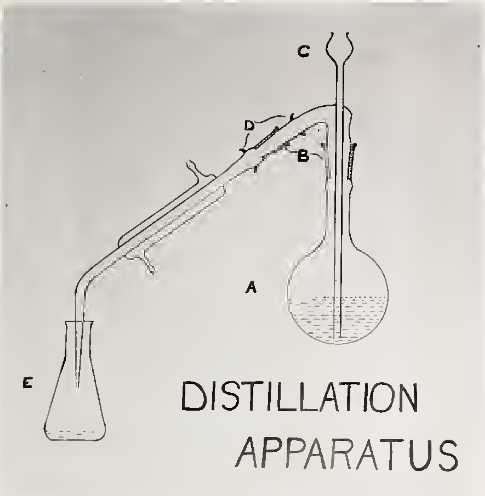

Figure 2

A is a 500 cc round bottom flask in which both the digestion and distillation were carried out. Flasks of larger or smaller capacity may be used.

At B are ground glass joints which connect the distilling flask to the adapter and the adapter to the condenser.

C is a thistle tube through which hydrobromic acid and bromine may be added prior to distillation.

D glass hooks, these aid in holding the ground joint together. Rubber bands are stretched from one set to the other.

E a 200 cc erlenmeyer flask is used as a receiver to catch the distillate.

Sulfur dioxide in slight excess was passed into the distillate in the erlenmeyer flask to reduce the bromine and precipitate the selenium.

$$SO_2 + SeBr_4 + 2H_2O \rightarrow Se\downarrow + 4\ HBr + H_2SO_4$$

Decolorization of bromine and precipitation of selenium was brought about with the aid of the apparatus shown in Fig. 3. It was merely a means of generating sulfur dioxide gas, utilizing it and having the excess drawn off to be used again or absorbed in an absorption train.

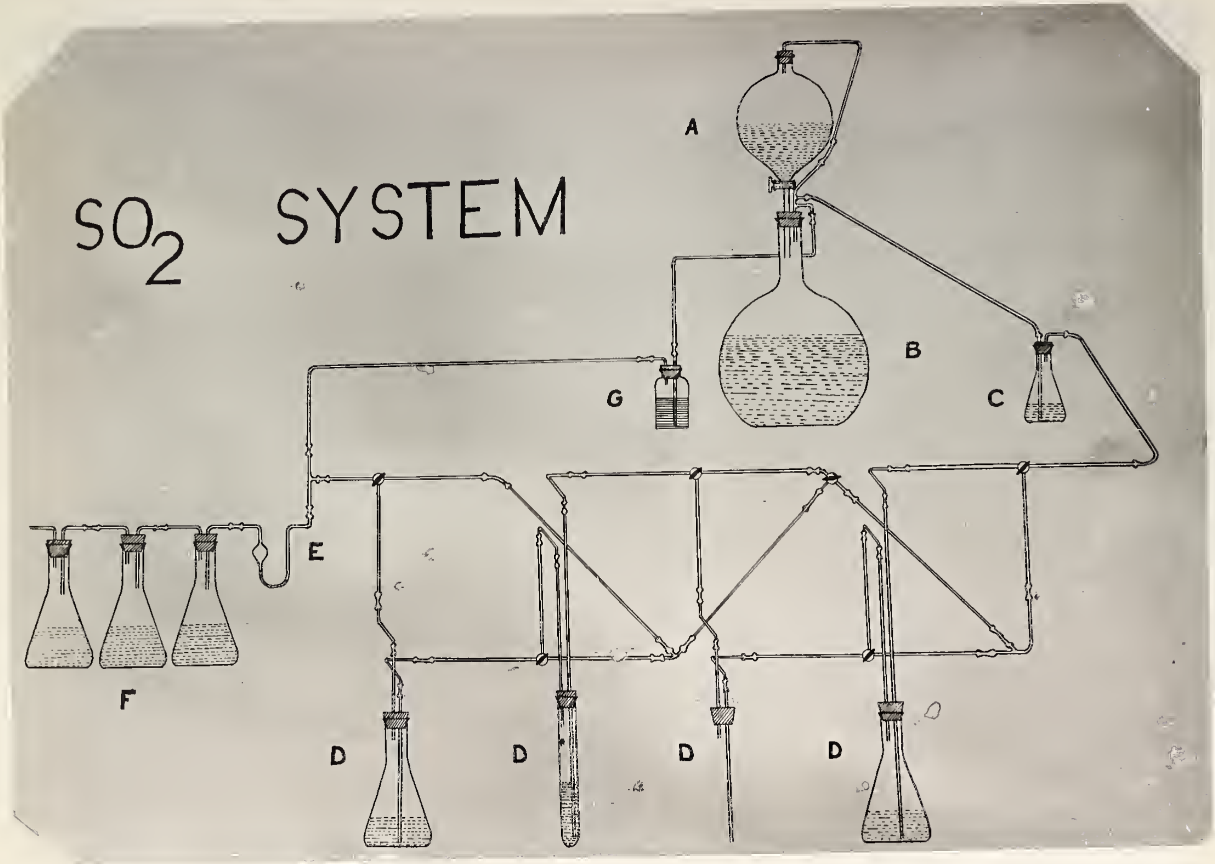

Figure 3

A is a dropping funnel which acts as a reservoir for sulfuric acid to be dropped into B which is a flask containing sodium sulfite suspension. The sulfur dioxide generated is dried by bubbling it through concentrated sulfuric acid in C after which it may be made to pass through any or all of the flasks at D. E is a bubble counter. F is an absorption train consisting of a series of flasks containing solutions of sodium hdyroxide in which any excess of sulfur dioxide is absorbed. G is a small safety jar containing about one and a quarter inches of mercury and through which sulfur dioxide may pass when the pressure in B becomes too great.

Approximately 0.25 grams of hydroxylamine hydrochloride was added to ensure complete precipitation of the selenium. The flask was stoppered loosely and allowed to stand overnight.

The precipitated selenium was collected on an asbestos mat in a gooch crucible and washed slightly with hydrobromic acid containing hydroxylamine hydrochloride. This selenium was redissolved by passing through it, in small portions, 10 cc of dilute hydrochloric acid containing an excess of bromine.

It was then reprecipitated in an 18 mm test tube with sulfur dioxide and hydroxylamine hydrochloride as in the earlier part of the experiment. The depth of color produced by the precipitated selenium was compared in about four hours with standards pptd with $SO_2$ containing 0.000; 0.003; 0.006; 0.009; 0.012; 0.015; 0.02; 0.03 m of selenium in similar 10 cc volumes. A stock solution of selenic acid was prepared containing 1 mg of selenium per cubic centimetre. For the purpose of making standards, a standard solution was made from this by diluting 10 cc of the stock solution to 1 litre

The comparison was found to be best carried out on both a black and on a white surface. Artificial light is unsatisfactory for the comparison. Occasionally an off color one is obtained but any of these were refiltered and determined with the next lot of determinations. Robinson (34) and others have recommended the addition of 1 cc of 5 per cent agar solution to the solutions before precipitation to prevent the selenium precipitating to the bottom of the tube. Since thisis of use mainly where fairly large amounts of selenium are present it was found unwarranted to use agar in the determination.

Blank runs showed that reagents used such as nitric, sulfuric, hydrobromic and hydrochloric acids, mercuric oxide and bromine were essentially free from selenium. The asbestos used in the gooch crucibles was washed with concentrated hydrochloric acid and bromine until clear filtrates could be obtained on washing bromine and acid through it.

Since large quantities of hydrobromic acid are needed in the distillation stage it was found necessary to effect recovery of the hydrobromic acid from the filtrates. This was accomplished by a process of fractional distillation in which the constant boiling acid of about 47 per cent was collected for use. Due to, what appeared to be, waxy substances in the grain distilling over with the hydrobromic acid it was not found possible to obtain a clear acid. These fatty materials were found to interfere somewhat with the precipitation of the selenium.

In attempting to clarify the hydrobromic acid the following things were tried.

a- The addition of excess bromine to the acid to be distilled gave only the first portion of the distillate clear.

b- The cloudy distillate was shaken with carbon tetrachloride with but slow and incomplete removal of the materials causing the trouble. Further the carbon tetrachloride remaining in the hydrobromic acid interferes with the precipitation of selenium.

c- If the material were in colloidal suspension the addition of such substances as sodium sulfate, alcohol and sodium sulfate, trichloracetic acid ought to discharge and dehydrate the particles so that coagulation would take place. These were found to be of no avail.

d- Precipitation of barium sulfate through the hydrobromic acid results in but slight clarification.

e- Saywell (57) clarified vinegar through the use of casein and tannin, casein and bentonite, potassium ferrocyanide and a protein such as gelatin or albumin. Of these substances a one-tenth per cent fresh bentonite suspension was found satisfactory in clarifying the hydrobromic acid. The bentonite was allowed to stand in contact overnight with the hydrobromic acid and then filtered off. The acid was fractionally distilled and the first one-third of constant boiling acid coming over was discarded.

The middle fractions were decolorized with sulfur dioxide and allowed to stand overnight to precipitate any selenium present. After filtration this acid was ready for use in the isolation of selenium.

## RESULTS

The results of the selenium analysis of wheat and soil samples are tabulated according to the location from which they came and the geological formation over which they lie. In cases where the exact location from which a sample came could not be obtained, the location of the nearest town was put down. For the purposes of examination, the federal electoral districts were found to be a convenient basis on which to subdivide the results of analysis of wheat samples. Graphically the results are shown divided on the arbitrary basis of samples containing more or less than 0.3 PPM of selenium. There is no logical basis for making the division at this point except that a certain percentage ofthe results in some areas seem to contain this amount or more, while samples from other regions, in general contain less than this amount.

The results of the analysis of soils for selenium are shown in Table 3 and graphically represented in Figure 4. Analysis of wheats are shown in Table 4 and Figure 5.

## TABLE 3 ANALYSIS OF SOIL SAMPLES

| LAB.NO. | TOWN | LOCATION | FORMATION | PPM Se. |
|---|---|---|---|---|
| 1 | Alliance | 15-40-13 W4 | Bearpaw | 0.0 |
| 10 | Banff | 12-26-12 W5 | Paleozoic | 0.0 |
| 7 | Blackfalds | 26-39-27 W4 | Paskapoo | 0.5 |
| 86 | Blairmore | 35-7-4 W5 | Lower Cret. | 0.1 |
| 16 | Brooks | 32-18-14 W4 | Bearpaw | 0.0 |
| 2 | Calgary | 15-24-1 W5 | Paskapoo | 0.0 |
| 87 | Champion | 7-15-23 W4 | Edmonton | 0.4 |
| 88 | Claresholm | 26-12-27 W4 | Paskapoo | 0.0 |
| 12 | Coutts | 4-1-15 W4 | Belly River | 0.9 |
| 6 | Delburne | 22-37-23 W4 | Paskapoo | 0.7 |
| 90 | Delburne | 22-27-23 W4 | Paskapoo | 0.0 |
| 84 | High River | 6-19-28 W4 | Paskapoo | 0.0 |
| 170 | Islay | 9-51-4 W4 | Belly River | 0.03 |
| 17 | Lethbridge | 31-8-21 W4 | Bearpaw | 0.0 |
| 171 | Lloydminster | 2-50-28 W3 | Upper Cret. | 0.0 |
| 3 | Loyalist | 16-35-6 W4 | Bearpaw | 0.0 |
| 14 | Manyberries | 24-5-6 W4 | Belly River | 0.0 |
| 15 | Medicine Hat | 31-12-5 W4 | Belly River | 0.5 |
| 13 | Nemiscam | 16-6-10 W4 | Belly River | 0.7 |
| 11 | Raymond | 8-6-20 W4 | Belly River | 0.0 |
| 9 | Raven | 14-36-4 W5 | Paskapoo | 0.5 |
| 5 | Red Deer | 16-38-27 W4 | Paskapoo | 0.2 |
| 89 | Spring Coulee | 33-4-23 W4 | Edmonton | 0.0 |
| 85 | Taber | 32-9-16 W4 | Belly River | 0.0 |
| 8 | Veteran | 18-35-8 W4 | Bearpaw | 0.0 |
| 172 | Wetaskiwin | 14-46-24 W4 | Edmonton | 0.2 |
| 4 | Youngstown | 4-29-9 W4 | Bearpaw | 0.0 |

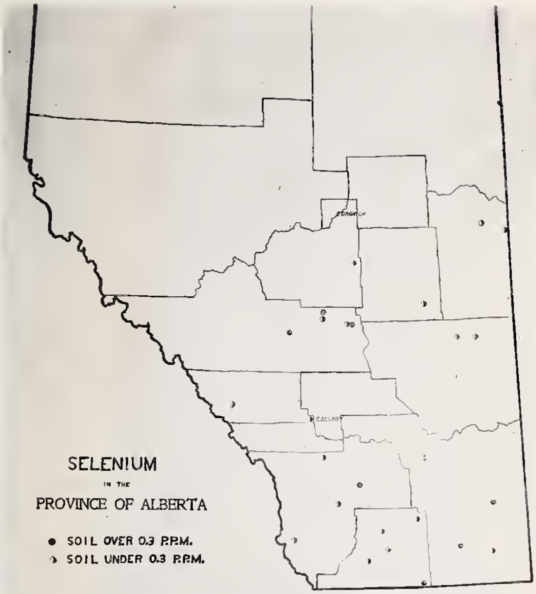
EDMONTON
CALGARY
SELENIUM
IN THE
PROVINCE OF ALBERTA
● SOIL OVER 0.3 P.P.M.
◑ SOIL UNDER 0.3 P.P.M.

Figure 4

Table 4 ANALYSIS OF WHEAT SAMPLES

## MEDICINE HAT CONSTITUENCY

| LAB.NO. | TOWN | LOCATION | FORMATION | PPM Se. |
|---|---|---|---|---|
| 145 | Bassano | 17-21-18 W4 | Bearpaw | .1 |
| 106 | Bingville | 2-18-7 W4 | Belly River | .9 |
| 134 | Bowmanton | 4-15-4 W4 | Belly River | 0.3 |
| 118 | Box Springs | 27-14-6 W4 | Belly River | 0.0 |
| 155 | Box Springs | 27-14-6 W4 | Belly River | 0.1 |
| 95 | Brooks | 32-18-14 W4 | Belly River | 0.1 |
| 146 | Bow Island | 36-10-11 W4 | Belly River | 0.2 |
| 113 | Burdette | 23-10-12 W4 | Belly River | 0.4 |
| 140 | Burdette | 23-10-12 W4 | Belly River | 0.0 |
| 92 | Dauntless | 12-11-6 W4 | Belly River | 0.0 |
| 139 | Duchess | 29-20-14 W4 | Bearpaw | 0.2 |
| 222 | Duchess | 29-20-14 W4 | Bearpaw | 0.0 |
| 133 | Dunmore | 1-12-5 W4 | Belly River | 0.0 |
| 148 | Dunmore | 1-12-5 W4 | Belly River | 0.0 |
| 149 | Dunmore | 1-12-5 W4 | Belly River | 0.1 |
| 154 | Dunmore | 1-12-5 W4 | Belly River | 0.0 |
| 112 | Eagle Butte | 36-7-4 W4 | Belly River | 0.0 |
| 109 | Foremost | 17-6-11 W4 | Belly River | 0.0 |
| 107 | Grantham | 8-13-15 W4 | Belly River | 0.0 |
| 102 | Grassy Lake | 16-10-13 W4 | Belly River | 0.2 |
| 108 | Grassy Lake | 16-10-13 W4 | Belly River | 0.0 |
| 105 | Hilda | 36-17-1 W4 | Belly River | 0.0 |
| 212 | Hilda | 36-17-1 W4 | Bearpaw | 0.0 |
| 104 | Irvine | 31-11-2 W4 | Belly River | 0.0 |
| 97 | Irvine | 31-11-2 W4 | Belly River | 0.7 |
| 114 | Irvine | 31-11-2 W4 | Belly River | 0.0 |
| 121 | Irvine | 33-11-3 W4 | Belly River | 0.1 |
| 127 | Irvine | 31-11-2 W4 | Belly River | 0.5 |
| 132 | Irvine | 31-11-2 W4 | Belly River | 0.4 |
| 18 | Jameson | 4-17-17 W4 | Edmonton | 0.0 |
| 141 | Manyberries | 24-5-6 W4 | Belly River | 0.0 |
| 91 | Medicine Hat | 31-12-5 W4 | Belly River | 0.0 |
| 110 | Medicine Hat | 31-12-5 W4 | Belly River | 0.0 |
| 117 | Medicine Hat | 18-8-5 W4 | Edmonton | 0.5 |
| 120 | Medicine Hat | 31-12-5 W4 | Belly River | 0,0 |
| 152 | Medicine Hat | 15-10-3 W4 | Bearpaw | 0.1 |
| 153 | Medicine Hat | 15-12-5 W4 | Belly River | 0.1 |
| 151 | Redcliff | 17-13-6 W4 | Belly River | 0.0 |
| 93 | Schuler | 9-16-1 W4 | Belly River | 0.3 |
| 144 | Millicent | 20-20-13 W4 | Bearpaw | 0.0 |
| 122 | Seven Persons | 1-11-7 W4 | Belly River | 0.2 |
| 233 | Strathmore | 21-23-25 W4 | Paskapoo | 0.0 |
| 111 | Suffield | 1-15-8 W4 | Belly River | 0.1 |

| LAB.NO. | TOWN | LOCATION | FORMATION | PPM Se. |
|---|---|---|---|---|
| 115 | Suffield | 34-14-9 W4 | Belly River | 0.0 |
| 123 | Suffield | 34-14-9 W4 | Belly River | 0.0 |
| 103 | Tilley | 19-17-12 W4 | Belly River | 0.5 |
| 119 | Tilley | 19-17-12 W4 | Belly River | 0.3 |
| 125 | Tilley | 19-17-12 W4 | Belly River | 0.3 |
| 221 | Tilley | 21-16-13 W4 | Belly River | 0.0 |
| 242 | Tilley | 21-16-13 W4 | Belly River | 0.1 |
| 232 | Morrin | 35-21-19 W4 | Bearpaw | 0.1 |
| 142 | Vauxhall | 10-13-16 W4 | Belly River | 0.3 |
| 116 | Walsh | 35-11-1 W4 | Belly River | 0.4 |
| 126 | Walsh | 35-11-1 W4 | Belly River | 0.1 |
| 128 | Walsh | 35-11-1 W4 | Belly River | 0.3 |
| 129 | Walsh | 35-11-1 W4 | Belly River | 1.0 |
| 143 | Walsh | 35-11-1 W4 | Belly River | 1.0 |
| 147 | Walsh | 35-11-1 W4 | Belly River | 0.2 |
| 131 | Whitla | 5-11-8 W4 | Belly River | 0.6 |
| 138 | Winnifred | 17-11-9 W4 | Belly River | 0.4 |

## LETHBRIDGE CONSTITUENCY

| LAB.NO. | TOWN | LOCATION | FORMATION | PPM Se. |
|---|---|---|---|---|
| 188 | Barons | 28-11-23 W4 | Edmonton | 0.1 |
| 247 | Barons | 27-11-23 W4 | Edmonton | 0.7 |
| 28 | Broxburn | 30-8 -20 W4 | Belly River | 0.0 |
| 156 | Broxburn | 30-8 -20 W4 | Belly River | 0.1 |
| 100 | Cardston | 9-3 -25 W4 | Paskapoo | 0.0 |
| 241 | Lethbridge | 31-8-21 W4 | Belly River | 0.1 |
| 226 | Maybutt | 5-7-18 W4 | Belly River | 0.1 |
| 124 | Monarch | 7-10-23 W4 | Edmonton | 0.0 |
| 30 | Nobleford | 3-11-23 W4 | Edmonton | 0.5 |
| 31 | Nobleford | 3-11-23 W4 | Edmonton | 0.6 |
| 94 | Nobleford | 3-11-23 W4 | Bearpaw | 0.4 |
| 157 | Nobleford | 3-11-23 W4 | Edmonton | 0.3 |
| 197 | Nobleford | 16-11-22W4 | Bearpaw | 0.1 |
| 96 | Taber | 32-9-16 W4 | Belly River | 0.1 |
| 130 | Taber | 32-9-16 W4 | Belly River | 0.0 |
| 150 | Taber | 32-19-16 W4 | Belly River | 0.1 |
| 98 | Welling | 17-6-21 W4 | Bearpaw | 0.2 |
| 227 | Wrentham | 36-6-17 W4 | Belly River | 0.1 |
| 249 | Weentham | 24-6-17 W4 | Belly River | 0.5 |
| 250 | Wrentham | 8-6-16 W4 | Belly River | 0.1 |
| 251 | Wrentham | 27-5-17 W4 | Belly River | 0.0 |
| 252 | Wrentham | 26-6-17 W4 | Belly River | 1.0 |
| 253 | Wrentham | 16-7-16 W4 | Belly River | 0.1 |
| 254 | Wrentham | 25-5-16 W4 | Belly River | 0.1 |
| 255 | Wrentham | 34-6-18 W4 | Belly River | 0.0 |

## MACLEOD CONSTITUENCY

| LAB.NO. | TOWN | LOCATION | | FORMATION | PPM Se. |
|---|---|---|---|---|---|
| 29 | Claresholm | 26-12-27 | W4 | Paskapoo | 0.5 |
| 192 | Claresholm | 20-12-27 | W4 | Paskapoo | 0.1 |
| 224 | Claresholm | 34-12-25 | W4 | Paskapoo | 0.0 |
| 101 | Glenwood | 12-5-27 | W4 | Paskapoo | 0.0 |
| 84 | High River | 6-19-28 | W4 | Paskapoo | 0.0 |
| 190 | High River | 18-18-1 | W4 | Paskapoo | 0.1 |
| 202 | High River | 19-18-28 | W4 | Paskapoo | 0.1 |
| 136 | Hillspring | 18-4-27 | W4 | Edmonton | 0.0 |
| 135 | Pincher | 22-6-30 | W4 | Paskapoo | 0.0 |
| 218 | Pincher Creek | 14-6-30 | W4 | Paskapoo | 0.1 |
| 207 | Pincher Creek | 23-5-29 | W4 | Edmonton | 0.1 |

## BATTLE RIVER CONSTITUENCY

| | | | | | |
|---|---|---|---|---|---|
| 215 | Barradale | 3-50-5 | W4 | Belly River | 0.1 |
| 191 | Chauvin | 35-44-1 | W4 | Belly River | 0.1 |
| 203 | Hardisty | 5-43-10 | W4 | Belly River | 0.0 |
| 216 | Hardisty | 6-43-9 | W4 | Belly River | 0.0 |
| 245 | Hardisty | 6-43-9 | W4 | Belly River | 0.2 |
| 246 | Hayter | 32-39-1 | W4 | Belly River | 0.1 |
| 43 | Innisfree | 3-51-11 | W4 | Belly River | 0.0 |
| 44 | Innisfree | 3-51-11 | W4 | Belly River | 0.0 |
| 45 | Innisfree | 3-51-11 | W4 | Belly River | 0.0 |
| 46 | Innisfree | 3-51-11 | W4 | Belly River | 0.0 |
| 170 | Islay | 9-51-4 | W4 | Belly River | 0.03 |
| 171 | Lloydminster | 28-50-2 | W4 | Belly River | 0.0 |
| 320 | Lloydminster | 32-50-1 | W4 | Belly River | 0.0 |
| 195 | Mannville | 6-50-8 | W4 | Belly River | 0.2 |
| 48 | Myrnam | 2-54-9 | W4 | Belly River | 0.0 |
| 49 | Myrnam | 2-54-9 | W4 | Belly River | 0.0 |
| 51 | Myrnam | 205409 | W4 | Belly River | 0.0 |
| 57 | Norway Valley | 16-55-5 | W4 | Upper Cret. | 0.0 |
| 19 | Provost | 16-39-2 | W4 | Belly River | 0.6 |
| 24 | Provost | 16-39-2 | W4 | Belly River | 0.0 |
| 240 | Provost | 32-50-6 | W4 | Belly River | 0.0 |
| 56 | Vermilion | 32-50-6 | W4 | Belly River | 0.0 |
| 58 | Vermilion | 19-48-6 | W4 | Belly River | 0.0 |
| 59 | Vermilion | 32-50-6 | W4 | Belly River | 0.0 |

## CAMROSE CONSTITUENCY

| | | | | | |
|---|---|---|---|---|---|
| 66 | Bruce | 25-48-15 | W4 | Bearpaw | 0.0 |
| 204 | Bruce | 11-48-15 | W4 | Bearpaw | 0.1 |
| 217 | Bruce | 11-48-15 | W4 | Bearpaw | 0.1 |
| 21 | Bulwark | 22-38-12 | W4 | Bearpaw | 0.0 |

| LAB.NO. | TOWN | LOCATION | FORMATION | PPM Se. |
|---|---|---|---|---|
| 200 | Bulwark | 34-18-12 W4 | Bearpaw | 0.0 |
| 210 | Castor | 30-38-13 W4 | Edmonton | 0.0 |
| 223 | Castor | 4-39-13 W4 | Bearpaw | 0.1 |
| 213 | Daysland | 8-44-14 W4 | Bearpaw | 0.2 |
| 229 | Daysland | 25-43-15 W4 | Edmonton | 0.1 |
| 244 | Daysland | 14-44-15 W4 | Edmonton | 0.0 |
| 225 | Gadsby | 20-39-16 W4 | Edmonton | 0.1 |
| 201 | Hardisty | 14-42-11 W4 | Belly River | 0.1 |
| 211 | Killam | 14-43-13 W4 | Bearpaw | 0.0 |
| 237 | Killam | 14-43-13 W4 | Bearpaw | 0.1 |
| 42 | Lavoy | 24-50-14 W4 | Belly River | 0.0 |
| 63 | Poe | 20-49-16 W4 | Bearpaw | 0.0 |
| 206 | Ryley | 6-50-17 W4 | Edmonton | 0.2 |
| 61 | Shants | 28-50-18 W4 | Edmonton | 0.0 |
| 37 | Stettler | 6-39-18 W4 | Edmonton | 0.6 |
| 38 | Stettler | 36-38-20 W4 | Edmonton | 0.6 |
| 62 | Tofield | 1-51-19 W4 | Edmonton | 0.0 |
| 236 | Viking | 26-46-14 W4 | Bearpaw | 0.0 |

## ACADIA CONSTITUENCY

| | | | | |
|---|---|---|---|---|
| 22 | Castor | 35-37-14 W4 | Edmonton | 0.0 |
| 23 | Castor | 32-38-12 W4 | Edmonton | 0.0 |
| 243 | Castor | 31-37-13 W4 | Edmonton | 0.0 |
| 208 | Cereal | 27-26-7 W4 | Bearpaw | 0.1 |
| 228 | Cereal | 27-26-7 W4 | Bearpaw | 0.0 |
| 239 | Chinook | 17-29-7 W4 | Bearpaw | 0.0 |
| 20 | Coronation | 13-36-11 W4 | Bearpaw | 0.0 |
| 25 | Coronation | 13-36-11 W4 | Bearpaw | 0.0 |
| 26 | Coronation | 13-36-11 W4 | Bearpaw | 0.0 |
| 27 | Coronation | 13-36-11 W4 | Bearpaw | 0.5 |
| 199 | Delia | 1-31-18 W4 | Edmonton | 0.0 |
| 209 | Delia | 1-31-18 W4 | Edmonton | 0.0 |
| 194 | DeWinton | 22-29-4 W4 | Bearpaw | 0.0 |
| 35 | Erskine | 22-37-31 W4 | Edmonton | 0.0 |
| 238 | Fleet | 30-36-12 W4 | Edmonton | 0.0 |
| 189 | Howie | 7-23-9 W4 | Bearpaw | 0.1 |
| 198 | Loyalist | 22-35-7 W4 | Bearpaw | 0.1 |
| 231 | Yemoor | 10-35-17 W4 | Edmonton | 0.4 |

## JASPER-EDSON CONSTITUENCY

| | | | | |
|---|---|---|---|---|
| 68 | Barrhead | 20-59-3 W4 | Edmonton | 0.0 |
| 70 | Barrhead | 20-59-3 W5 | Edmonton | 0.0 |
| 74 | Barrhead | 33-59-5 W5 | Edmonton | 0.0 |
| 75 | Barrhead | 20-59-3 W5 | Edmonton | 0.0 |
| 165 | Cherhill | 9-56-5 W5 | Edmonton | 0.0 |

| LAB.NO. | TOWN | LOCATION | FORMATION | PPM Se. |
|---|---|---|---|---|
| 79 | Glenevis | 34-55-4 W5 | Edmonton | 0.0 |
| 83 | Greencourt | 14-58-9 W5 | Edmonton | 0.0 |
| 78 | Lac St Anne | 4-54-3 W5 | Edmonton | 0.3 |
| 72 | Legal | 9-57-24 W4 | Edmonton | 0.0 |
| 67 | Manola | 1-59-3 W5 | Edmonton | 0.0 |
| 69 | Manola | 1-59-3 W5 | Edmonton | 0.0 |
| 81 | Mayerthorpe | 21-57-8 W5 | Edmonton | 0.0 |
| 160 | Mellowdale | 22-60-3 W5 | Edmonton | 0.0 |
| 90 | Onoway | 35-54-2 W5 | Edmonton | 0.3 |
| 162 | Onoway | 14-55-2 W5 | Edmonton | 0.0 |
| 76 | Peavey | 4-57-2 W5 | Edmonton | 0.0 |
| 168 | Rochfort | 5-57-7 W5 | Edmonton | 0.0 |
| 82 | Sangudo | 36-56-7 W5 | Edmonton | 0.0 |
| 166 | Sangudo | 36-56-7 W5 | Edmonton | 0.0 |
| 161 | Spruce Grove | 2-53-27 W4 | Edmonton | 0.0 |
| 47 | Stony Plain | 1-53-1 W5 | Edmonton | 0.0 |
| 73 | Vimy | 38-58-25 W4 | Edmonton | 0.2 |

### PEACE RIVER CONSTITUENCY

| | | | | |
|---|---|---|---|---|
| 159 | Clairmont | 16-72-7 W6 | Upper Cret. | 0.4 |
| 174 | Donnelly | 1-78-21 W5 | Upper Cret. | 0.0 |
| 175 | Donnelly | 1-77-21 W5 | Upper Cret. | 0.0 |
| 185 | Dreau | 11-78-22 W5 | Upper Cret. | 0.0 |
| 178 | Enilda | 13-74-16 W5 | Upper Cret. | 0.1 |
| 176 | Falher | 4-78-21 W5 | Upper Cret. | 0.2 |
| 163 | Girousville | 11-78-22 W5 | Upper Cret. | 0.0 |
| 177 | Girouxville | 16-78-22 W5 | Upper Cret. | 0.0 |
| 179 | High Prairie | 24-74-17 W5 | Upper Cret. | 0.3 |
| 180 | High Prairie | 24-74-17 W5 | Upper Cret. | 0.2 |
| 182 | High Prairie | 24-74-17 W5 | Upper Cret. | 0.2 |
| 183 | High Prairie | 24-74-17 W5 | Upper Cret. | 0.2 |
| 186 | High Prairie | 24-74-17 W5 | Upper Cret | 0.1 |
| 187 | High Prairie | 24-74-17 W5 | Upper Cret. | 0.3 |
| 164 | Judah | 35-82-22 W5 | Upper Cret. | 0.1 |
| 181 | Judah | 35-82-22 W5 | Upper Cret. | 0.1 |
| 184 | | 35-82-22 W5 | Upper Cret. | 0.1 |

### MISCELLANEOUS GROUP CONSISTING OF THE VEGREVILLE, ATHABASCA, WETASKIWIN, RED DEER, BOW RIVER, and CALGARY CONSTITUENCIES

| | | | | |
|---|---|---|---|---|
| 34 | Airdrie | 36-27-1 W5 | Paskapoo | 0.0 |
| 39 | Airdrie | 36-27-1 W5 | Paskapoo | 0.4 |
| 158 | Ardrossan | 2-53-22 W4 | Edmonton | 0.2 |
| 169 | Calmar | 15-49-26 W4 | Edmonton | 0.0 |
| 64 | Chipman | 30-54-18 W4 | Bearpaw | 0.0 |
| 32 | Clyde | 21-59-25 W4 | Edmonton | 0.2 |
| 219 | Elnora | 15-35-22 W4 | Paskapoo | 0.1 |

| LAB.NO. | TOWN | LOCATION | FORMATION | PPM Se. |
|---|---|---|---|---|
| 84 | High River | 6-19-28 W4 | Paskapoo | 0.0 |
| 193 | Lamont | 16-55-19 W4 | Bearpaw | 0.1 |
| 235 | Midnapore | 20-22-1 W5 | Paskapoo | 0.0 |
| 36 | Mirror | 28-40-22 W4 | Edmonton | 0.0 |
| 60 | Mundare | 16-53-16 W4 | Bearpaw | 0.0 |
| 33 | Red Deer | 6-38-27 W4 | Paskapoo | 0.0 |
| 40 | Sylvan Lake | 32-38-1 W5 | Paskapoo | 0.0 |
| 41 | Sylvan Lake | 32-38-1 W5 | Paskapoo | 0.0 |
| 214 | Three Hills | 8-31-22 W5 | Paskapoo | 0.2 |
| 167 | Treton | -49-26 W4 | Edmonton | 0.0 |
| 196 | Vegreville | 23-51-15 W4 | Belly River | 0.2 |
| 220 | Vegreville | 28-51-16 W4 | Belly River | 0.0 |
| 52 | Vilna | 24-58-13 W4 | Edmonton | 0.0 |
| 53 | Vilna | 20-59-13 W4 | Edmonton | 0.0 |
| 54 | Vilna | 32-58-11 W4 | Edmonton | 0.0 |
| 55 | Vilna | 32-58-11 W4 | Edmonton | 0.0 |
| 205 | Wolf Creek | 10-54-16 W4 | Belly River | 0.0 |
| 65 | Westlock | 28-59-27 W4 | Edmonton | 0.0 |
| 71 | Westlock | 34-60-27 W4 | Edmonton | 0.0 |
| 77 | Westlock | 27-60-24 W4 | Edmonton | 0.1 |
| 173 | Wetaskiwin | 14-46-24 W4 | Edmonton | 0.06 |

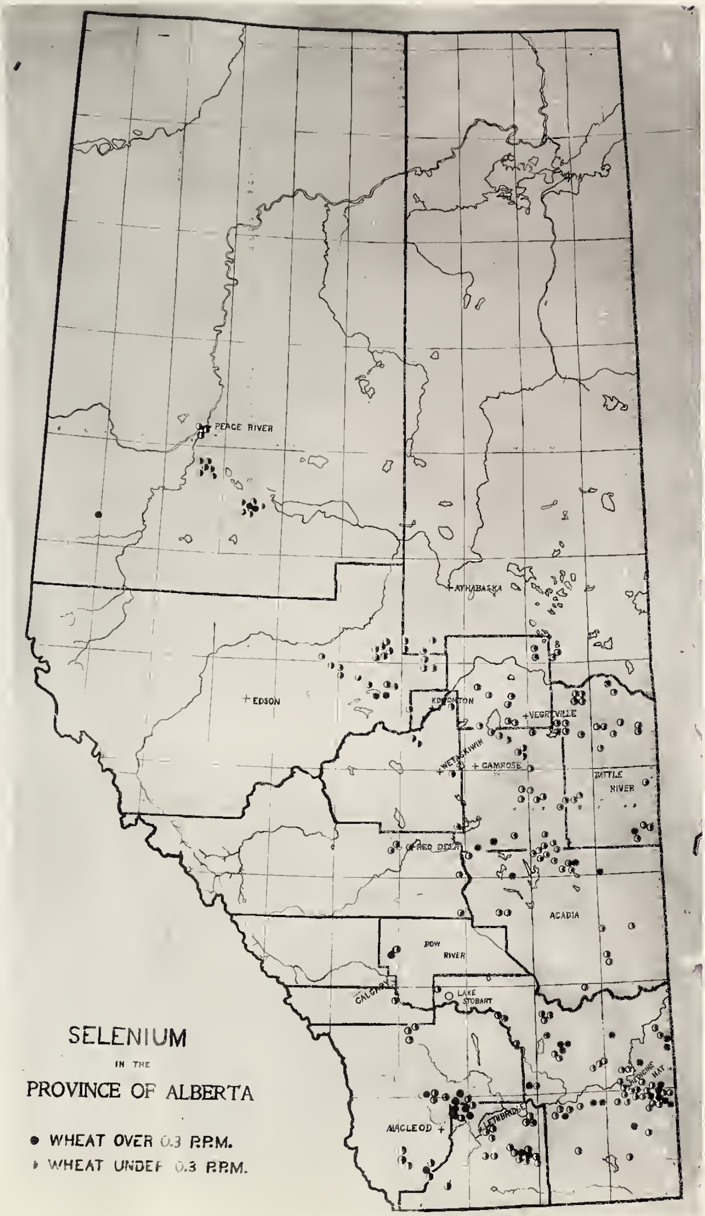
SELENIUM
IN THE
PROVINCE OF ALBERTA
● WHEAT OVER 0.3 P.P.M.
◐ WHEAT UNDER 0.3 P.P.M.
PEACE RIVER
ATHABASKA
EDSON
EDMONTON
VEGREVILLE
WETASKIWIN
CAMROSE
BATTLE RIVER
RED DEER
ACADIA
BOW RIVER
CALGARY
LAKE STOBART
MEDICINE HAT
MACLEOD
LETHBRIDGE

Figure 5

The results of the analysis of the soils and wheats are summarized below in Table 5.

TABLE 5

| Constituenci(es) | | Number of Samples Examined | Number Over 0.3 PPM | Percentage Over 0.3 PPM |
|---|---|---|---|---|
| Medicine Hat (Wheats) | | 61 | 17 | 28% |
| Lethbridge | " | 25 | 6 | 24% |
| Macleod | " | 11 | 1 | 9% |
| Acadia | " | 18 | 2 | 11% |
| Battle River | " | 25 | 1 | 4% |
| Camrose | " | 21 | 2 | 10% |
| Jasper-Edson | " | 22 | 2 | 9% |
| Peace River | " | 17 | 3 | 17% |
| Miscellaneous Group | " | 28 | 1 | 4% |
| All of the Soils | | 27 | 7 | 26% |

Ten litres of a sample of water from Lake Stobart were evaporated to dryness after being made alkaline with sodium peroxide. Selenium in the residue was determined after distillation with hydrobromic acid and bromine. Less than 0.2 parts per billion were found. The symptoms of western duck sickness are very alike those of selenium

poisoning (Twomey (59)). On this basis it has been thought by some that selenium in the water might account for the death of large numbers of ducks in the neighborhood of Lake Stobart. The low concentration obtained would indicate that some other agent than selenium is the cause of the sickness. The work of Shaw (60) would indicate that the death of the ducks is probably due to Clostridium botulinum Type C. The low concentration of selenium found is in accord with the findings of other workers who have determined selenium in water. (58) (25).

The suspended matter that had settled out of the sample of water was analyzed for selenium. In 9.5 grams no selenium could be detected.

## DISCUSSION OF RESULTS

### A- Soils

It can be seen from Table 3 that the most selenium found in any soil amounted to only 0.9 PPM. In work carried out by Byers (25) and Moxon (30) in some of the American states the maximum values obtained were much higher. Byers reports values from 0.0 to over 80 PPM, while Moxon has values as high as 40 PPM.

It must be kept in mind that the number of soil samples examined is very small and for that reason one cannot say that samples with higher selenium content do not exist in the province. If this limitation is kept in mind it can be concluded that the samples tested will not grow grains which are highly seleniferous. Moxon states that soils containing more than 0.5 PPM of selenium are potentially dangerous. Out of the 27 soils examined six at Blackfalds, Coutts, Delburne, Medicine Hat, Nemiscam and Raven had a concentration of selenium this large or more. These six soils may be regarded as potentially dangerous but undoubtedly the selenium content in plants grown on these soils will not be nearly so high as on similar soils containing

80 PPM as found in some of the American soils.

It was shown early by Franke (61) and others that the areas best known to produce toxic grain were on soils derived mainly from the Pierre and related shales of the Upper Cretaceous period. The geological formations in Alberta which correspond to the Pierre are the Bearpaw shales and the Belly River sandstone. Many of the soils with the higher selenium content are on the soil overlying the Belly River sandstone. The low values obtained from other soils on these same formations is undoubtedly due to that the greater part of Alberta is covered with glacial drift, and there are only a few localities in which the surface soil is derived from the underlying rock. For this reason it might be expected that there are few localities in Alberta where the selenium content of the soil is high.

B- Wheat

The majority of the wheat samples examined came from the southern part of the province. On examination of the results it can be seen that the greatest amount of selenium in any sample was 1 PPM. As earlier stated the minimal toxic concentration

in foodstuffs is 4 PPM. For these reasons the selenium content of none of the wheats examined in Alberta are capable of producing the symptoms of alkali disease. Since only the seed has been examined no conclusions can be drawn with regard to the selenium content of other portions of the same plant nor of other plants grown on the same soil.

As can be seen from the results many of the samples showing the highest selenium content were grown on soils overlying the Belly River formation. In general, the grains grown on the soils over the Bearpaw shale gave low values for selenium. Reasons mentioned before, that is, the presence of greater or less thicknesses of glacial drift, lead one to the conclusion that it is very difficult to compare the selenium content of the grain with the underlying strata of rock.

Although there appears to be no immediate selenium problem in this province, field investigations should be undertaken to determine any areas supporting native plants generally found in association with seleniferous soils. Such an examination may bring to light restricted areas which are toxic.

## SUMMARY

The methods for the detection and estimation of selenium have been reviewed and in many cases work has been done in order to determine whether they give accurate results when used for the determination of selenium in wheat and soils.

The analytical method which was adopted has been described in detail.

Twenty seven soils have been examined. Six of these showed a selenium concentration in excess of 0.5 PPM and for this reason may be regarded as potentially dangerous.

Two hundred and twenty eight samples of wheat grown in many parts of the province have been analyzed for selenium and the results of these analyses are reported. No evidence was obtained of toxic wheats being grown in Alberta.

# ACKNOWLEDGEMENT

The writer wishes to express his sincere appreciation and gratitude to Dr. O.J. Walker for his helpful advice and assistance during the carrying out of this research.

Grateful acknowledgement is made to the Department of Field Crops and to Mr. J.A. Morrison for their aid in the collection of samples.

Grateful acknowledgement is made to the Board of Governors of the University of Alberta for a Research Scholarship which enabled the writer to carry on this investigation.

## REFERENCES

1. Larsen, White and Bailey, South Dakota Expt. Sta. Bull. 132, Page 220, (1912)
2. Larsen and Bailey, South Dakota Expt. Sta. Bull. 147, Page 299 (1913).
3. Moxon, South Dakota Expt. Sta. Bull. 311, (1937).
4. Byers, U.S. Dept. Agric. Tech. Bull. 482, (1935).
5. Marco Polo, "The Travels of Marco Polo" Grosset Dunlap, New York, Book First, Chap. 43, P.68.
6. Beath, Draize and Gilbert, Wyo. Expt. Sta. Bull. 200 (1934).
7. Franke and Potter, Science, 83, 330, (1936).
8. Schneider, Science, 83, 32, (1936).
9. Franke, Journal Nutrition, 8, 597, (1934).
10. Franke and Tully, Poultry Science, 14, 273, (1935).
11. Beath and Draize, J. Am. Vet. Med. Assoc. 86, 753, (1935).
12. Beath, Science, 81, 617, (1935).
13. Beath and Draize, Wyo. Expt. Sta. Annual Report, 43 annual, Page 14, (1932-33).
14. Munsell, De Vaney and Kennedy, U.S. Dept. of Agric. Tech. Bull. 534, (1936).
15. Martin, Am. Jour. Bot. 23, 471, (1936).
16. Jones, Biochemical Jour. 4, 405, (1909).
17. Franke and Painter, Cereal Chemistry, 15, 1, (1938)
18. Robinson, Jour. Assoc. Off. Agric. Chem., 16, 423, (1933).
19. Franke, Jour. Nutrition, 10, 205, (1935).
20. Byers, U.S. Dept. Agric. Tech. Bull. 530, (1936).

21. Miller and Byers, Jour. Agric. Res., 55, 59, (1937).

22. Hurd-Karrer, Jour. Agric. Res. 50, 413, (1935).

23. Hurd-Karrer, Jour. Agric. Res. 54, 601, (1937).

24. Martin and Trelease, Am. Jour. Bot. 25, 380, (1938).

25. Byers, Miller, Williams and Lakin, U.S. Dept. Agric. Tech. Bull., 601, (1938).

26. Williams and Byers, Ind. Eng. Chem., 28, 912, (1936).

27. Williams and Byers, Ind. Eng. Chem. Anal. Ed. 6, 296, (1934).

28. Franke and Painter, Jour. Nutrition, 10, 599, (1935).

29. Robinson, Ind. Eng. Chem. 28, 736, (1936).

30. Jones, Horn and Gersdorff, Cereal Chem., 14, 130, (1937).

31. Beath, Eppson and Gilbert, WYoming Agric. Expt. Sta. Bull, 206 (1935).

32. Smith and Westfall, U.S. Pub. Health Rep., 51, 1496, (1936).

33. Wilcox, Country Gentleman, 8, 105, (193 )

34. Robinson, Dudley, Williams and Byers, Ind. Eng. Chem. Anal. Ed., 6, 274, (1934).

35. Robinson, J., Assoc. Off. Agric. Chem., 16, 423, (1933).

36. Robinson, Ind. Eng. Chem., 28, 736, (1936).

37. Dudley and Byers, Ind. Eng.Chem. Anal. Ed., 7, 3, (1935).

38. Williams and Lakin, Ind. Eng. Chem. Anal. Ed., 7 409, (1935).

39. Curl and Osborn, J. Assoc. Off. Agric. Chem., 21, 228, (1938).

40. Osborn and Krasnitz, J. Assoc. Off. Agric. Chem., 17, 339, (1934).

41. Hovorka, Coll. Czeck. Chem. Comm., 4, 300, (1932).

42. Kheraskova and Veisbrut Z. Anal. Chem., 102, 353, (1935).

43. Evans, Amm. Mineral. 22, 1128, (1931).

44. Deniges, Bull. Soc. Pharm., 75, 197, (1937).

45. Feigl and Demant Mikrochim Acta, 1, 322, (1933).

46. Cousen, J. Soc. Glass, Tech., 7, 303, (1923).

47. Hoverka, Coll. Czeck. Chem. Comm., 7, 125, (1935).

48. Berg and Teitelbaum Mikrochim Emich Festschr, 23, (1930).

49. Saccardi and Martini Chim. Ind. Agr. Biol., 13, 210, (1937).

50. Ljung, Ind. Eng. Chem. Anal. Ed., 9, 328, (1937).

51. Hall, Ind. Eng. Chem. Anal. Ed., 10, 395, (1938).

52. Ivanov, Chem. Ztg., 32, 468, (1908).

53. Pierson Ind. Eng. Chem. Anal. Ed., 11, 86, (1939).

54. Pierson, Ind. Eng. Chem. Anal. Ed., 11, 86, (1939).

55. Horn, Ind. Eng. Chem. Anal. Ed., 6, 34, (1934).

56. Mellor, "A Comprehensive Treatise on Inorganic and Theoretical Chemistry", Vol. X, Page 748, Longmans Green & Co., 1930.

57. Saywell, Ind. Eng. Chem. Ind. Ed., 26, 379, (1934).

58. Miller and Byers, Ind. Eng. Chem. News Ed., 13, 456, (1935).

59. Twomey and Twomey, 83, 470, (1936).

60. Shaw, J. Bact., 32, 79, (1936).

61. Franke, Rice, Johnson and Schoening, U.S. Dept. Agric. Circular, 320, (1934).

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